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STABILITY OF NITRATE-ION CONCENTRATIONS IN SIMULATED DEPOSITION SAMPLES USED FOR QUALITY-ASSURANCE ACTIVITIES BY THE U.S. GEOLOGICAL SURVEY

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4042

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By Timothy C. Willoughby, Randolph B. See,
and LeRoy J. Schroder

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4042

Denver, Colorado
1989

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CONVERSION FACTORS

Metric (International System) units used in this report may be converted to inch-pound units by the use of the following conversion factors:

Multiply metric unit	By	To obtain inch-pound unit
centimeter (cm)	0.3937	inch
gram (g)	0.0353	ounce
liter (L)	1.057	quart, liquid
micrometer (μm)	3.904×10^{-4}	inch
milligram (mg)	3.530×10^{-5}	ounce
milliliter (mL)	0.0338	ounce, fluid

Temperature can be converted from degree Celsius (^{o}C) to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F=9/5\ ^{o}C+32$$

The following terms and abbreviations also are used in this report:

Megohm per centimeter (MΩ/cm) is equal to 1×10^{6} ohms per centimeter

Milligram per liter (mg/L)

STABILITY OF NITRATE-ION CONCENTRATIONS IN SIMULATED DEPOSITION SAMPLES USED FOR QUALITY-ASSURANCE ACTIVITIES BY THE U.S. GEOLOGICAL SURVEY

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ABSTRACT

Three experiments were conducted to determine the stability of nitrate-ion concentrations in simulated deposition samples. In the four experiment-A solutions, nitric acid provided nitrate-ion concentrations ranging from 0.6 to 10.0 milligrams per liter and that had pH values ranging from 3.8 to 5.0. In the five experiment-B solutions, sodium nitrate provided nitrate-ion concentrations ranging from 0.5 to 3.0 milligrams per liter, and the pH was adjusted to about 4.5 for each of the solutions by addition of sulfuric acid. In the four experiment-C solutions, nitric acid provided nitrate-ion concentrations ranging from 0.5 to 3.0 milligrams per liter. Major cation and anion concentrations were added to each solution to simulate natural deposition.

Aliquots were removed from the 13 solutions and analyzed by ion chromatography about once a week for 100 days to determine if any changes occurred in nitrate-ion concentrations throughout the study period. No substantial changes were observed in the nitrate-ion concentrations in solutions that had initial concentrations less than 4.0 milligrams per liter in experiments A and B, although most of the measured nitrate-ion concentrations for the 100-day study were slightly less than the initial concentrations. In experiment C, changes in nitrate-ion concentrations were much more pronounced; the measured nitrate-ion concentrations for the study period were less than the initial concentrations for 62 of the 67 analyses.

INTRODUCTION

The U.S. Geological Survey's acid-rain project has several external quality-assurance programs, which the U.S. Geological Survey operates for the National Atmospheric Deposition Program and the National Trends Network (NADP/NTN). During the past several years, the U.S. Geological Survey has needed to develop simulated deposition samples that have stable nitrate-ion concentrations to be used in blind-audit and interlaboratory

comparison programs (See and others, 1988). Fishman and others (1986) reported that the only acceptable technique for the preservation of nitrogen species in natural water and in tap water, for as long as 16 days, was to add mercuric chloride and to chill at 4 °C. The U.S. Geological Survey's acid-rain project needs simulated deposition samples that have a shelf life of at least 100 days. The addition of mercuric chloride and chilling of the samples was not practical for quality-assurance samples used for simulated deposition. Mercuric chloride interfered with the methods used for analysis of wet deposition, and chilling the samples continuously for 100 days was not possible at all NADP/NTN deposition-collection sites.

The purpose of this report is to: (1) Describe the methods used to produce simulated deposition samples that have stable nitrate-ion concentrations for use in quality-assurance activities; (2) determine if simulated deposition samples with stable nitrate-ion concentrations can be produced; and (3) examine the effects of varying nitrate-ion concentrations and pH on the stability of nitrate-ion concentrations in simulated deposition samples.

APPROACH

Simulated deposition samples were prepared to provide a variety of nitrate concentrations and pH values for three experiments. Nitric acid or sodium nitrate was used to provide the nitrate-ion concentrations that were similar to concentrations present in natural deposition. The simulated deposition samples were analyzed about once a week for 100 days by ion chromatography to detect changes, if any, in nitrate-ion concentrations.

Design of Experiments

The effect of pH on the stability of nitrate-ion concentrations in simulated deposition samples was examined in experiment A. A nitric acid stock solution was prepared by diluting 1 mL of reagent-grade nitric acid to 1 L using ultrapure (greater than 16.7 MΩ/cm) water that had been passed through a filter with a pore diameter of 0.2 micrometer. Four 2-L solutions that had target pH values of 3.8, 4.2, 4.6, and 5.0 were prepared by further dilution of the appropriate volumes of nitric acid stock solution with ultrapure water. These solutions hereafter will be referred to as A3.8, A4.2, A4.6, and A5.0. Two 250-mL aliquots were removed from each of the four solutions to be used for duplicate analyses. If changes were detected in nitrate-ion concentrations in a solution during the study period, a comparison could be made using the duplicate aliquots, to determine if the changes were due to contamination of a single aliquot or if the solution had changed systematically.

In experiment B, the stability of nitrate-ion concentrations was examined in solutions that had varying nitrate-ion concentrations and a constant pH. A sodium nitrate stock solution was prepared by diluting 0.686 g of sodium nitrate to 1 L, using ultrapure water. A sulfuric acid stock solution was prepared by diluting 1 mL of reagent-grade acid to 1 L, using ultrapure water. Five 2-L solutions that had target nitrate-ion concentrations of 0.5, 1.0, 1.5, 2.0, and 3.0 mg/L were prepared by further dilution of the appropriate volumes of the sodium nitrate stock solution and 2.10 mL of the sulfuric acid stock solution with ultrapure water. These solutions hereafter will be referred to as B0.5, B1.0, B1.5, B2.0, and B3.0. The addition of the sulfuric acid adjusted the pH of each solution to 4.5. Sulfuric acid also was added as a preservative (Kopp and McKee, 1979); however, the concentration of sulfuric acid needed for preservation of nitrogen species is much larger than was used in this experiment. Two 250-mL aliquots were removed from each of the five solutions to be used for duplicate analyses.

In experiment C, the stability of nitrate-ion concentrations was examined in solutions that contained calcium, magnesium, potassium, sodium, chloride, and sulfate concentrations that were comparable to those in natural deposition. Four 1-L stock solutions were prepared by dilution of the following quantities of reagent-grade salts with ultrapure water: (1) 0.191 g of potassium chloride, (2) 0.392 g of magnesium chloride, (3) 0.286 g of calcium sulfate, and (4) 1.487 g of sodium sulfate. Four 2-L solutions that had target nitrate-ion concentrations of 0.5, 1.0, 2.0, and 3.0 mg/L were prepared by further diluting 1 mL of the potassium chloride stock solution, 1 mL of the magnesium chloride stock solution, 1 mL of the sodium sulfate stock solution, 10 mL of the calcium sulfate stock solution, and the appropriate volumes of the nitric acid stock solution, prepared in experiment A, to 2 L with ultrapure water. These solutions hereafter will be referred to as C0.5, C1.0, C2.0, and C3.0. Two 250-mL aliquots were removed from each of the four solutions to be used for duplicate analyses.

Prior to removing the two 250-mL aliquots, each of the 13 solutions from the three experiments was analyzed in triplicate. All analyses were done using a Dionex 2000i[1] ion chromatograph, that had a Dionex AS4A separator column and a 0.5 mL sample loop (Dionex Corporation, 1985). Each of the 250-mL aliquots then were analyzed about once a week, beginning 7 days after the solutions were prepared and continuing for 100 days.

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[1]Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Preparation of Sample Solutions

All chemicals used were of reagent-grade quality or better. The solid reagents were dried at 104 °C for 24 hours prior to weighing. All of the glass and plastic ware were cleaned prior to use by rinsing three times with at least 50 mL of ultrapure water, then the glass or plastic ware was filled with ultrapure water and allowed to stand for 24 hours. The bottles and flasks then were emptied and rinsed at least three more times using 50 mL or more of ultrapure water immediately before use. No detergents or acid-leaching techniques were used in the cleaning process.

Each of the 13 solutions was prepared in a class A, 2-L volumetric flask. The volumes of the stock solutions added and the target pH values or nitrate-ion concentrations for the 13 solutions are listed in tables 1 through 3.

Table 1.--Volumes of nitric acid stock solution diluted to 2 liters with ultrapure water to obtain the target pH values for the four solutions in experiment A

Solution label	Volume of nitric acid stock solution diluted to 2 liters (milliliters)	Target pH (units)
A3.8	19.98	3.8
A4.2	7.95	4.2
A4.6	3.17	4.6
A5.0	1.26	5.0

Table 2.--Volumes of sodium nitrate stock solution added to 2.10 milliliters of the sulfuric acid stock solution and diluted to 2 liters with ultrapure water to obtain the target nitrate-ion concentrations for the five solutions in experiment B

Solution label	Volume of sodium nitrate stock solution diluted to 2 liters (milliliters)	Target nitrate-ion concentration (milligrams per liter)
B0.5	2.00	0.5
B1.0	4.00	1.0
B1.5	6.00	1.5
B2.0	8.00	2.0
B3.0	12.00	3.0

Table 3.--Volumes of nitric acid stock solution added to 1 milliliter each of the potassium chloride, magnesium chloride, and sodium sulfate stock solutions, and to 10 milliliters of the calcium sulfate stock solution, and diluted to 2 liters to obtain the target nitrate-ion concentrations for the four solutions in experiment C

Solution label	Volume of nitric acid stock solution diluted to 2 liters (milliliters)	Target nitrate-ion concentration (milligrams per liter)
C0.5	1.02	0.5
C1.0	2.03	1.0
C2.0	4.07	2.0
C3.0	6.10	3.0

Each of the 13 solutions then was transferred to a 2-L, high-density polyethylene bottle. Three 5-mL subsamples were removed from each of the 13 solutions and were analyzed by ion chromatography to verify the dilutions. The two 250-mL aliquots then were removed from each of the 2-L bottles containing the 13 solutions and were transferred to two 250-mL polyethylene bottles.

STABILITY OF NITRATE-ION CONCENTRATIONS

The mean and standard deviation of the results obtained from the 13 solutions, which were measured in triplicate prior to removal of the two 250-mL aliquots, are listed in table 4. Hereafter, the mean measured concentrations for the three analyses done for each of the solutions will be referred to as the initial concentrations.

A total of 233 analyses was made during the 100-day study using the 26 aliquots. The results for the paired aliquots from the same solution were combined. Nine nitrate analyses -- three from experiment A, two from experiment B, and four from experiment C -- were determined to be outliers when a Grubbs Test (Grubbs, 1950) was made using the data set for each of the 13 solutions. After outliers were removed from the data set, a total of 224 analyses remained from the three experiments.

Table 4.--Target and mean measured (initial) nitrate-ion concentrations for the 13 solutions

Solution label	Target concentration of nitrate-ion (milligrams per liter)	Mean measured concentration of nitrate-ion (milligrams per liter)	Standard deviation (milligrams per liter)
A3.8	9.98	9.91	0.02
A4.2	3.97	3.90	.05
A4.6	1.58	1.50	.06
A5.0	.63	.58	.01
B0.5	.50	.47	.01
B1.0	1.00	.99	.07
B1.5	1.50	1.46	.01
B2.0	2.00	1.95	.02
B3.0	3.00	2.94	.03
C0.5	.50	.57	.04
C1.0	1.00	1.05	.17
C2.0	2.00	2.00	.09
C3.0	3.00	3.00	.07

Experiment A--Effects of Variable pH

Except for the solution A3.8 (the solution that had the largest nitrate-ion concentration and the smallest pH), there was no effect on the nitrate-ion concentrations during the 100-day study when pH was varied in experiment A. A plot of the measured nitrate-ion concentrations for experiment A compared to the number of days from solution preparation is shown in figure 1. The measured mean nitrate-ion concentrations, standard deviations, and the initial nitrate-ion concentrations for each of the four solutions in experiment A are listed in table 5.

The standard deviation for the measured mean nitrate-ion concentrations, for the 100-day study, in the four original solutions increased as the initial nitrate-ion concentration of the solution increased. This increase in variability was probably due to an increase in solution handling as the initial nitrate-ion concentration in the solutions increased; however, the relative standard deviation remained relatively constant. Solution A3.8 was diluted one part to five parts, and solution A4.2 was diluted one part to two parts before analyzing.

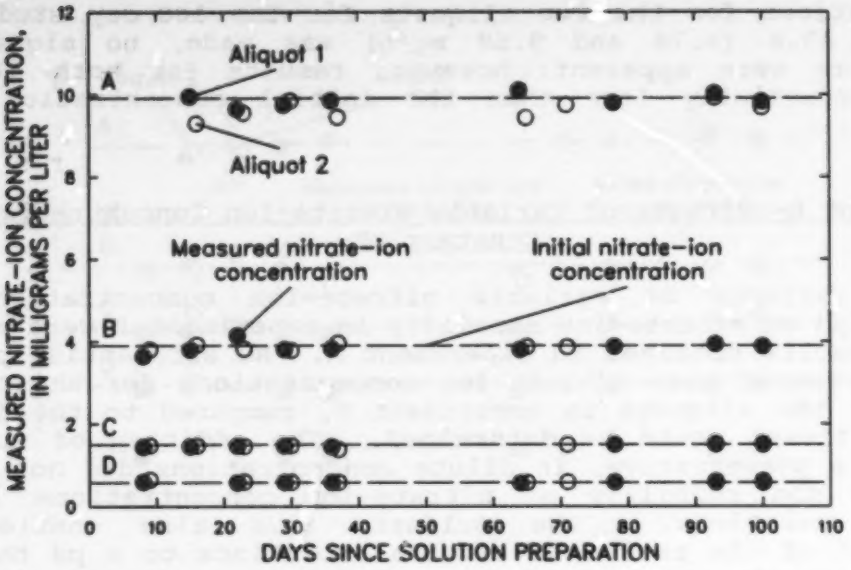

Figure 1.--Measured nitrate-ion concentrations as a function of the number of days since the preparation of the four solutions (A-D) in experiment A.

Table 5.--Measured mean and standard deviation of nitrate-ion concentrations for experiment A compared to the initial concentrations

Sample label	Measured mean concentration (milligrams per liter)	Standard deviation (milligrams per liter)	Initial concentration (milligrams per liter)
A3.8	9.68	0.27	9.98
A4.2	3.84	.07	3.90
A4.6	1.47	.04	1.50
A5.0	.59	.04	.58

When a comparison between the mean measured nitrate-ion concentrations for the two aliquots for the 100-day study from solution A3.8 (9.78 and 9.58 mg/L) was made, no significant differences were apparent; however, results for both aliquots were substantially less than the initial concentration (9.98 mg/L).

Experiment B--Effects of Variable Nitrate-Ion Concentrations and Constant pH

The effects of variable nitrate-ion concentrations and constant pH on nitrate-ion stability in experiment B were similar to the results obtained in experiment A. No substantial changes in the measured mean nitrate-ion concentrations for the 100-day study for the aliquots in experiment B, compared to the initial concentrations, could be determined. The addition of sulfuric acid, as a preservative, in dilute concentrations did not affect adversely the stability of nitrate-ion concentrations in the original solutions. The sulfuric acid also enabled the adjustment of the pH in the original solutions to a pH that was more consistent with natural deposition. The solutions B2.0 and B3.0 were diluted one part to two parts before analysis; this dilution probably resulted in greater variability in the measured mean nitrate-ion concentrations during the 100-day study. A plot of the measured nitrate-ion concentrations for experiment B compared to the number of days from solution preparation is shown in figure 2. The measured mean nitrate-ion concentrations and their standard deviations and how they compared to the initial concentrations are listed in table 6.

Experiment C--Effects of Major Cation and Anion Concentrations

The effects of major cation and anion concentrations on nitrate-ion stability in experiment C did not produce results similar to experiments A and B. In experiment C, the measured mean nitrate-ion concentrations were much smaller than the expected concentrations of the solutions, except for solution C2.0 (table 7). Solution C2.0 was the only solution in experiment C that had a nitrate-ion concentration within one standard deviation of the initial concentration. A plot of the measured nitrate-ion concentrations compared to the number of days from solution preparation is shown in figure 3. A comparison between the two aliquots was done for each solution from experiment C, and no substantial differences were apparent between the two aliquots, except for solution C2.0. The greater difference between the two aliquots for solution C2.0 probably was due to contamination of one of the aliquots.

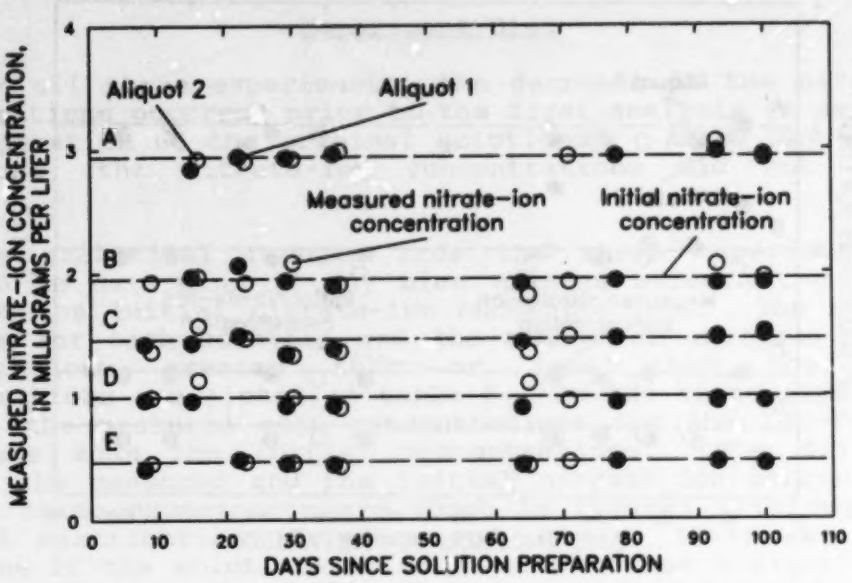

Figure 2.--Measured nitrate-ion concentrations as a function of the number of days since the preparation of the five solutions (A-E) in experiment B.

Table 6.--Measured mean and standard deviation of nitrate-ion concentrations for experiment B compared to the initial concentrations

Sample label	Measured mean concentration (milligrams per liter)	Standard deviation (milligrams per liter)	Initial concentration (milligrams per liter)
B0.5	0.46	0.02	0.47
B1.0	.97	.07	.99
B1.5	1.44	.07	1.46
B2.0	1.95	.09	1.95
B3.0	2.95	.06	2.94

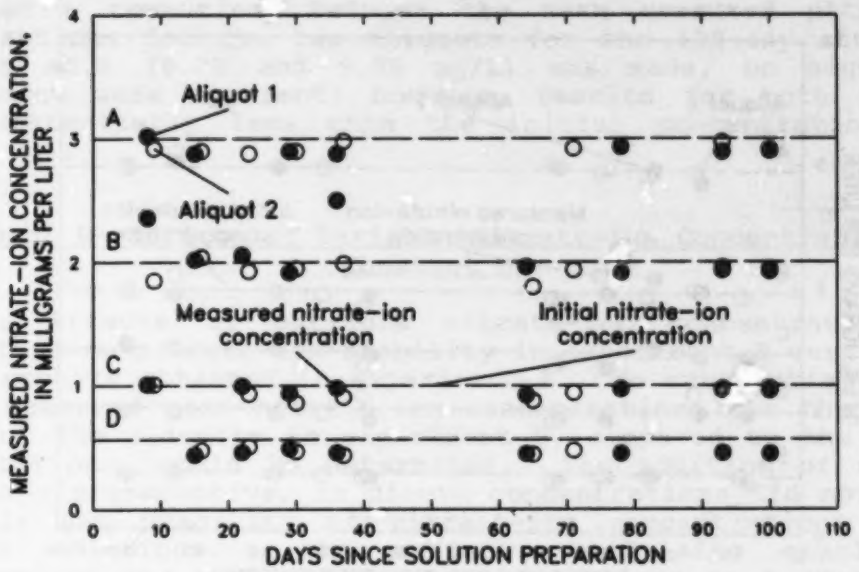

Figure 3.--Measured nitrate-ion concentrations as a function of the number of days since the preparation of the four solutions (A-D) in experiment C.

Table 7.--Measured mean and standard deviation of nitrate-ion concentrations for experiment C compared to the initial concentrations

Sample label	Measured mean concentration (milligrams per liter)	Standard deviation (milligrams per liter)	Initial concentration (milligrams per liter)
C0.5	0.46	0.02	0.57
C1.0	.95	.04	1.05
C2.0	1.97	.12	2.00
C3.0	2.91	.05	3.01

Experiment Bias

For all three experiments, the decrease in the nitrate-ion concentrations occurred prior to the first analysis (8 days after the preparation of the original solutions). After day 8 of the experiment, the nitrate-ion concentrations did not seem to change.

The analytical results from the three experiments were reviewed to determine if any bias existed between the measured mean and the initial nitrate-ion concentrations. The number of analyses for each solution and the number of analyses that had concentrations greater than or less than the initial concentrations are listed in table 8. In the three experiments, most of the measured mean concentrations for the 100-day study were less than the initial concentrations. The differences between the measured and the initial nitrate-ion concentrations for the three experiments are shown in figures 4 through 6. A binomial distribution (Friedman and others, 1983) was used to determine if the solutions in an experiment had a significant (α = 0.01) positive or negative bias when compared to the initial concentration. Only experiment C (the solutions that had major cation and anion concentrations added to represent natural deposition) had a statistically significant bias; 62 of the 67 measured nitrate-ion concentrations were less than the initial concentrations. Experiments A and B were determined to have no bias; however, most of the measured nitrate-ion concentrations for both experiments were less than the initial concentrations.

Table 8.--Results of test for bias, using a binomial distribution (Friedman and others, 1983)

[--, no bias determined]

Experiment	Number of analyses	Number of analyses that had nitrate-ion concentrations equal to or greater than the initial concentration	Number of analyses that had nitrate-ion concentrations less than the initial concentration	Determined to be biased	Positive or negative bias
A	69	25	44	No	--
B	88	30	58	No	--
C	67	5	62	Yes	Negative

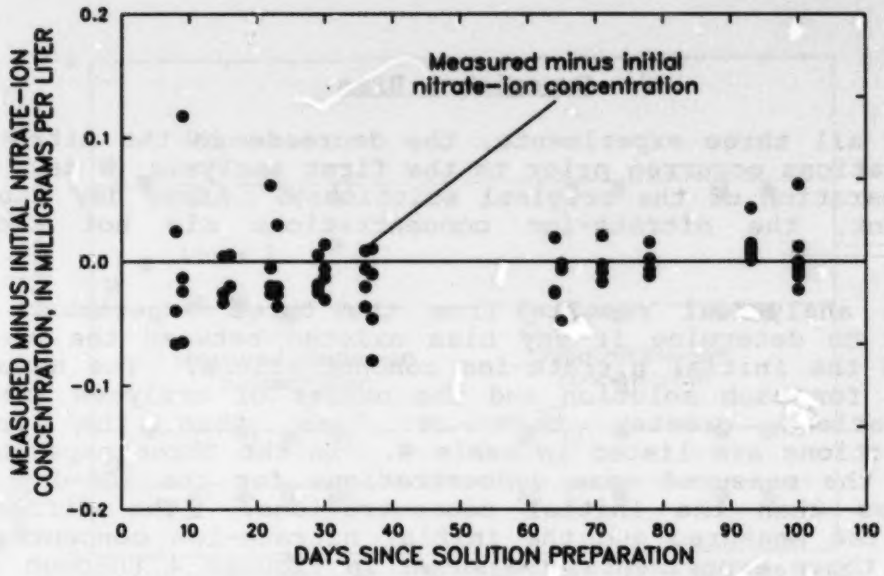

Figure 4.--Difference between the measured nitrate-ion and the initial nitrate-ion concentrations as a function of the number of days since the preparation of the four solutions in experiment A.

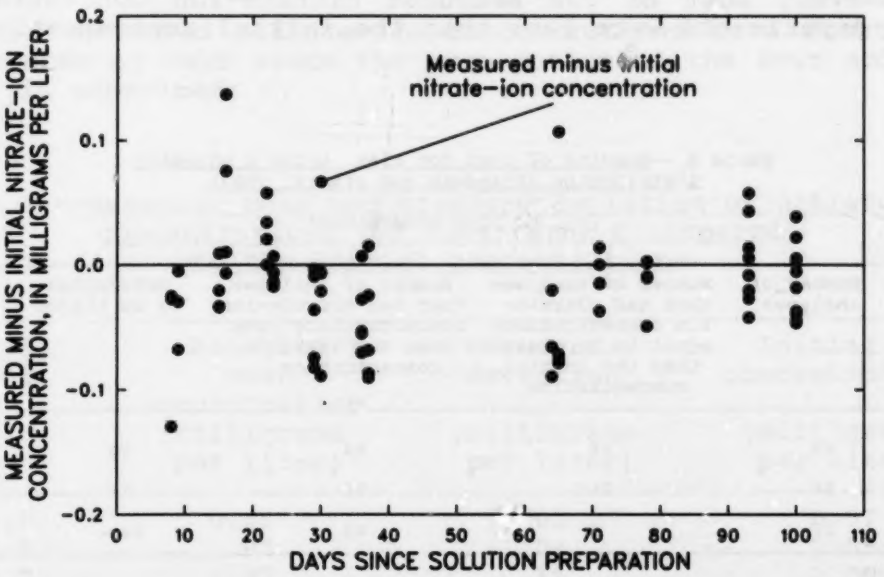

Figure 5.--Difference between the measured nitrate-ion and the initial nitrate-ion concentrations as a function of the number of days since the preparation of the five solutions in experiment B.

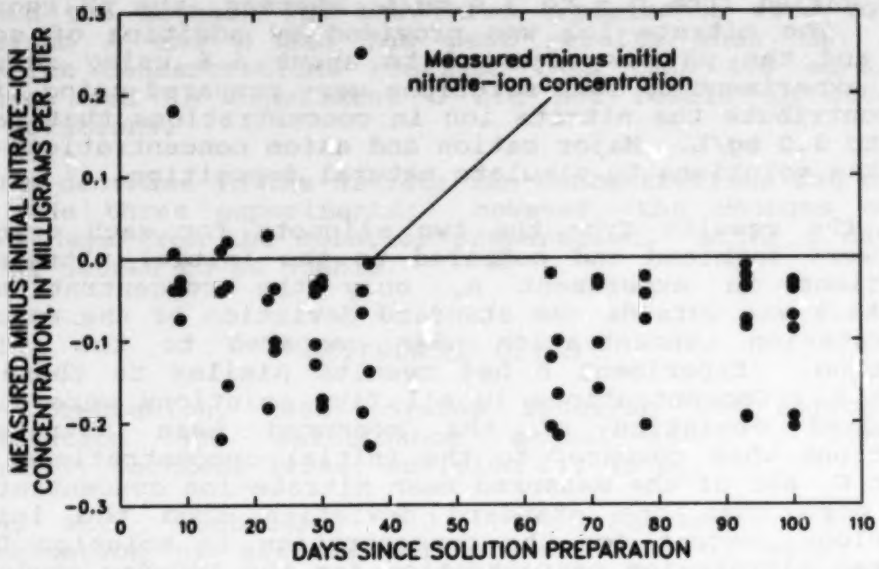

Figure 6.--Difference between the measured nitrate-ion and the initial nitrate-ion concentrations as a function of the number of days since the preparation of the four solutions in experiment C.

When the methods for the three experiments were compared, experiments A and B had the smallest amount of bias when the pH was adjusted to less than 4.0. The methods for experiment C did not result in acceptably stable solutions, possibly because of increased biological contamination introduced by addition of the potassium chloride, magnesium chloride, sodium sulfate, and calcium sulfate salt solutions. The addition of these salt solutions to make the solutions resemble natural deposition may have increased the biological activity, resulting in more extensive changes in the nitrate-ion concentrations.

SUMMARY AND CONCLUSIONS

Three experiments were conducted to determine the stability of nitrate-ion concentrations in simulated deposition samples for use in quality-assurance activities. Thirteen solutions were prepared with a considerable range of nitrate-ion concentrations and pH values; these solutions were analyzed about once a week during a 100-day study.

In experiment A, the effect of pH on the stability of nitrate-ion concentrations was examined using four solutions that ranged in pH from 3.8 to 5.0. Nitric acid was used to contribute the nitrate ion in concentrations ranging from 0.6 to 10.0 mg/L. In experiment B, the nitrate-ion concentrations in the five

solutions varied from 0.5 to 3.0 mg/L, whereas, the pH remained constant. The nitrate ion was provided by addition of sodium nitrate, and the pH was adjusted to about 4.5 using sulfuric acid. In experiment C, four solutions were prepared using nitric acid to contribute the nitrate ion in concentrations that ranged from 0.5 to 3.0 mg/L. Major cation and anion concentrations were added to the solutions to simulate natural deposition.

When the results from the two aliquots for each original solution were combined and compared to the initial nitrate-ion concentrations in experiment A, only the concentration in solution A3.8 was outside one standard deviation of the measured mean nitrate-ion concentration when compared to the initial concentration. Experiment B had results similar to those for experiment A. Concentrations in all five solutions were within one standard deviation of the measured mean nitrate-ion concentrations when compared to the initial concentrations. In experiment C, all of the measured mean nitrate-ion concentrations deviated more than one standard deviation from the initial concentrations, except for the concentration in solution C2.0. The measured nitrate-ion concentration for the 100-day study for solution C2.0 had more scatter than that in the other solutions. When the two aliquots from solution C2.0 were compared, a large difference was apparent. The difference between the two aliquots probably was due to contamination of one of the aliquots.

When a binomial distribution was used, measured nitrate-ion concentrations for the 100-day study in experiment A were determined to be not biased when compared to the initial concentrations; however, 64 percent of the concentrations were slightly less than the initial concentrations in the original solutions, which indicated that some changes in the nitrate-ion concentrations had occurred. The measured mean nitrate-ion concentrations in experiment B were more representative of the initial concentration than those from experiment A. No bias was detected between the measured and the initial concentrations when a binomial distribution was used to test for bias in experiment B. As in experiment A, most of the measured mean nitrate-ion concentrations were less than the initial concentrations (66 percent); however, the changes were not statistically significant. Bias was indicated between the measured nitrate-ion concentrations and the initial concentrations in experiment C; 62 of the 67 concentrations were less than the expected concentrations.

The difference in the results in experiment C, when compared to the other two experiments may be a result of additional biological contamination in the solutions. The addition of several more components to make the solutions resemble natural deposition may have resulted in increased biological activity, which then resulted in more extensive changes in the nitrate-ion concentrations.

When the methods for the three experiments were compared, experiments A and B had the best results when the initial nitrate-ion concentrations remained less than 4.0 mg/L. The procedure used in experiment C did not result in acceptably stable solutions.

Some decrease in the nitrate-ion concentrations can occur in any of the three experiments; however, the changes occurred within 8 days from the solution preparation. After 8 days, the solutions seemed to be stable.

REFERENCES CITED

Dionex Corporation, 1985, System 2000i/sp ion chromatograph operation and maintenance manual--1985: Sunnyvale, Calif., Document 32584, Revision 01, 49 p.

Fishman, M.J., Schroder, L.J., and Shockey, M.W., 1986, Evaluation of methods for preservation of water samples for nutrient analysis: International Journal of Environmental Studies, v. 26, no. 3, p. 231-238.

Friedman, L.C., Bradford, W.L., and Peart, D.B., 1983, Application of binomial distributions to quality assurance of quantitative chemical analyses: Journal of Environmental Science and Health, v. A18, no. 4, p. 561-570.

Grubbs, F.E., 1950, Sample criteria for testing outlying observations: Annals of Mathematical Statistics, v. 21, no. 3, p. 27-58.

Kopp, J.F., and McKee, G.D., 1979, Methods for chemical analysis of water and wastes (3d ed.): Cincinnati, Ohio, U.S. Environmental Protection Agency report, EPA-600/4-79-020, 460 p.

See, R.B., Schroder, L.J., and Willoughby, T.C., 1988, External quality-assurance results for the National Atmospheric Deposition Program and the National Trends Network during 1986: U.S. Geological Survey Water-Resources Investigations Report 88-4007, 15 p.

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